

55

B14

JK 43.546

1972
international book year



KFKI-72-72

1st part 1.

Á. I. Kiss

J. Szőke

QUANTUMSPECTROSCOPY

No 7. Pi-electron SCF-MO calculations
for disubstituted benzene derivatives
containing two acceptor groups

Part two: Numerical results of calculations

Hungarian Academy of Sciences

CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS



BUDAPEST

QUANTUMSPECTROSCOPY

Papers in this series:

1. A.I. Kiss and J. Szőke: Pi-Electron SCF-MO calculations for Monosubstituted Derivatives of Benzene
Chem. Phys. Lett. 11, 52 /1971/ and KFKI-72-1
2. A.I. Kiss and J. Szőke: Theoretical Investigation of Electronic Spectra of Monosubstituted Benzene Derivatives
Hung. Chem. Acta 1972, 74, 59 and KFKI-72-2
3. A.I. Kiss and J. Szőke: Pi-Electron SCF-MO calculations for Disubstituted Benzene Derivatives Containing Two Donor Groups
Part one: Discussion of Results.
Submitted to Chem. Phys. Lett., and KFKI-72-58
4. A.I. Kiss and J. Szőke: Pi-Electron SCF-MO Calculations for Disubstituted Benzene Derivatives Containing Two Donor Groups
Part two: Numerical Results of Calculations
KFKI-72-58
5. A.I. Kiss, A. Martin and J. Szőke: Singlet Transition Energies, MIM Wave Functions, PPP Charge Densities and Bond Orders of the Mono-and Disubstituted Halogenbenzenes
KFKI-72-73
6. A.I. Kiss and J. Szőke: Pi-Electron SCF-MO Calculations For Disubstituted Benzene Derivatives Containing Two Acceptor Groups
Part One: Discussion of Results
Submitted to Chemical Physics Letters, and KFKI-72-71
7. A.I. Kiss and J. Szőke: Pi-Electron SCF-MO Calculations For Disubstituted Benzene Derivatives Containing Two Acceptor Groups
Part two: Numerical Results of Calculations
KFKI-72-72

**PI-ELECTRON SCF-MO CALCULATIONS FOR DISUBSTITUTED
BENZENE DERIVATIVES CONTAINING TWO ACCEPTOR GROUPS**

Part Two:

Numerical Results of Calculations

A.I. Kiss

**Department of Physical Chemistry
Technical University, Budapest, Hungary**

and

J. Szőke

**Department of Optical Spectroscopy
Central Research Institute for Physics, Budapest, Hungary**

ABSTRACT

The π -electronic structures and spectra of disubstituted benzene derivatives containing carbonyl, carboxy, and nitro groups have been calculated by the Pariser-Parr-Pople method. For all disubstituted derivatives the same starting parameters, determined from the spectra of the monosubstituted compounds, were used. The calculations give good results for the singlet transition energies as well as for the ground state charge densities and bond orders.

РЕЗЮМЕ

Методом Паризера-Парра-Паппа были вычислены π -электронные структуры и спектры двузамещенных производных бензола, содержащих карбонильную, карбоксильную и нитро группы. Для расчетов каждого двузамещенного производного были использованы одинаковые исходные параметры, определенные из спектров однозамещенных производных. Хорошие результаты были найдены для энергии синглетных переходов, а также для распределения плотности зарядов и порядков связи в основном состоянии.

KIVONAT

Karbonil-, karboxil- és nitro-csoportot tartalmazó diszubsztituált benzolszármazékok π -elektronszerkezetét és szinképét számítottuk Pariser-Parr-Pople módszerrel. Minden diszubsztituált származékot azonos, a monoszubsztituált származékok szinképe alapján meghatározott kiindulási értékekkel számítottunk. A számítások jó eredménnyel adták a szinglet átmenetek energiáját, valamint az alapállapotú töltéssűrűség- és kötésrend-értékeket.

CONTENTS

1. CALCULATED AND EXPERIMENTAL SPECTRAL DATA	1
2. REFERENCES	5
3. CHARGE DENSITIES AND BOND ORDERS	6
3.1 Benzaldehyde	6
3.2 Benzoic acid	6
3.3 Nitrobenzene	6
3.4 Benzene-dialdehydes	7
3.5 Formylbenzoic acids	8
3.6 Nitrobenzaldehydes	9
3.7 Benzene-dicarboxylic acids	10
3.8 Nitrobenzoic acids	11
3.9 Dinitrobenzenes	12
4. CORRELATIONS BETWEEN THE CALCULATED AND EXPERIMENTAL TRANSITION ENERGIES	13
Fig. 4.1 Correlation between the calculated and ex- perimental energy of the α band	13
Fig. 4.2 Correlation between the calculated and ex- perimental energy of the p band	14

1.0	INTRODUCTION	1
2.0	GENERAL INFORMATION	2
3.0	DESIGNATION	3
4.0	DESCRIPTION	4
5.0	CONSTRUCTION	5
6.0	OPERATION	6
7.0	MAINTENANCE	7
8.0	REPAIRS	8
9.0	TESTING	9
10.0	SAFETY	10
11.0	ENVIRONMENTAL	11
12.0	CONCLUSION	12
13.0	APPENDICES	13
14.0	REFERENCES	14
15.0	INDEX	15
16.0	GLOSSARY	16
17.0	FIGURES	17
18.0	TABLES	18
19.0	FORMS	19
20.0	NOTES	20
21.0	REVISIONS	21
22.0	REVISIONS	22
23.0	REVISIONS	23
24.0	REVISIONS	24
25.0	REVISIONS	25
26.0	REVISIONS	26
27.0	REVISIONS	27
28.0	REVISIONS	28
29.0	REVISIONS	29
30.0	REVISIONS	30
31.0	REVISIONS	31
32.0	REVISIONS	32
33.0	REVISIONS	33
34.0	REVISIONS	34
35.0	REVISIONS	35
36.0	REVISIONS	36
37.0	REVISIONS	37
38.0	REVISIONS	38
39.0	REVISIONS	39
40.0	REVISIONS	40
41.0	REVISIONS	41
42.0	REVISIONS	42
43.0	REVISIONS	43
44.0	REVISIONS	44
45.0	REVISIONS	45
46.0	REVISIONS	46
47.0	REVISIONS	47
48.0	REVISIONS	48
49.0	REVISIONS	49
50.0	REVISIONS	50
51.0	REVISIONS	51
52.0	REVISIONS	52
53.0	REVISIONS	53
54.0	REVISIONS	54
55.0	REVISIONS	55
56.0	REVISIONS	56
57.0	REVISIONS	57
58.0	REVISIONS	58
59.0	REVISIONS	59
60.0	REVISIONS	60
61.0	REVISIONS	61
62.0	REVISIONS	62
63.0	REVISIONS	63
64.0	REVISIONS	64
65.0	REVISIONS	65
66.0	REVISIONS	66
67.0	REVISIONS	67
68.0	REVISIONS	68
69.0	REVISIONS	69
70.0	REVISIONS	70
71.0	REVISIONS	71
72.0	REVISIONS	72
73.0	REVISIONS	73
74.0	REVISIONS	74
75.0	REVISIONS	75
76.0	REVISIONS	76
77.0	REVISIONS	77
78.0	REVISIONS	78
79.0	REVISIONS	79
80.0	REVISIONS	80
81.0	REVISIONS	81
82.0	REVISIONS	82
83.0	REVISIONS	83
84.0	REVISIONS	84
85.0	REVISIONS	85
86.0	REVISIONS	86
87.0	REVISIONS	87
88.0	REVISIONS	88
89.0	REVISIONS	89
90.0	REVISIONS	90
91.0	REVISIONS	91
92.0	REVISIONS	92
93.0	REVISIONS	93
94.0	REVISIONS	94
95.0	REVISIONS	95
96.0	REVISIONS	96
97.0	REVISIONS	97
98.0	REVISIONS	98
99.0	REVISIONS	99
100.0	REVISIONS	100

Table 1.

1. CALCULATED AND EXPERIMENTAL SPECTRAL DATA

Compound	Calculated			Experimental ^{a/}			Ref.
	E(eV)	f	α°	E(eV)	log ϵ	f	
BENZALDEHYDE	4.526	0.026	111.1	4.460	2.97	0.022	1
	5.166	0.575	191.6	5.155	4.03	0.257	
	6.244	0.398	279.7				
	6.547	0.648	195.1				
BENZOIC ACID	4.643	0.016	119.2	4.525	3.02	0.025	1
	5.380	0.509	11.8	5.367	4.20	0.384	
	6.159	0.010	44.3				
	6.489	0.720	95.4				
NITROBENZENE	4.564	0.029	90.0	4.320	3.08	0.029	1
	5.067	0.418	0.0	4.949	3.97	0.224	
	5.899	0.018	270.0				
	6.080	0.289	90.0	5.961	3.99	0.235	
BENZENE-O-DIALDEHYDE	4.253	0.060	236.5	4.174	3.36	0.055	2
	4.726	0.324	142.6	4.862	3.95	0.214	
	5.650	1.156	221.4				
	5.945	0.268	302.0				
	6.826	0.015	205.2				
	6.881	0.009	355.9				
BENZENE-M-DIALDEHYDE	4.319	0.017	161.1	4.275	3.18	0.036	3
	5.095	0.257	248.9	5.166	4.11	0.309	
	5.345	1.149	156.3	5.510	4.15	0.339	
	5.787	0.366	40.0				
	6.785	0.113	353.9				
	6.995	0.296	250.0				
BENZENE-P-DIALDEHYDE	4.230	0.060	297.0				
	4.741	0.920	14.2				
	6.090	0.000	70.5				
	6.225	0.478	277.1				
	6.290	0.000	269.6				
	6.588	0.840	192.9				
O-FORMYLBENZOIC ACID	4.353	0.040	220.7	4.492	2.93	0.020	4
	4.841	0.272	309.9	5.535	3.90	0.192	
	5.700	0.060	244.6				
	5.742	1.118	214.6				
	6.206	0.633	104.2				
	6.648	0.007	59.1				
	7.001	0.032	326.3				
	7.261	0.126	39.6				

Table 1. Continued/

Compound	Calculated			Experimental ^{a/}			Ref.
	E (eV)	f	α^0	E (eV)	log ϵ	f	
M-FORMYLBENZOIC ACID	4.374	0.019	182.1				
	5.154	0.333	285.7				
	5.504	0.986	167.1				
	5.923	0.335	43.7				
	6.100	0.119	329.7				
	6.408	0.184	280.2				
	6.956	0.239	297.3				
	7.047	0.369	237.5				
P-FORMYLBENZOIC ACID	4.320	0.052	300.4	4.305	3.29	0.047	4
	4.819	0.858	14.1	4.979	4.24	0.420	
	5.788	0.033	116.1				
	6.189	0.360	273.2				
	6.289	0.039	271.7				
	6.570	0.528	174.4				
	6.649	0.459	213.7				
	7.031	0.091	284.4				
O-NITROBENZALDEHYDE	4.301	0.084	59.4	4.217	3.22	0.040	1
	4.772	0.309	142.4				
	5.450	0.094	183.2	5.019	3.85	0.170	
	5.618	0.755	226.3				
	5.842	0.141	313.0				
	6.496	0.121	81.8				
	6.686	0.048	328.4				
	6.775	0.530	278.0				
M-NITROBENZALDEHYDE	4.399	0.011	130.3	4.290	3.02	0.025	1
	5.062	0.178	206.5	5.081	4.00	0.240	
	5.351	0.987	147.2	5.510	4.01	0.245	
	5.662	0.155	201.8				
	5.942	0.310	87.4				
	6.270	0.045	274.8				
	6.656	0.247	225.2				
	6.946	0.212	302.5				
P-NITROBENZALDEHYDE	4.286	0.056	102.5	4.174	3.37	0.056	1
	4.796	0.753	187.1	4.805	3.97	0.224	
	5.619	0.082	90.5				
	5.959	0.076	250.0				
	5.971	0.010	166.5				
	6.369	0.309	286.1				
	6.574	0.751	191.4				

/Table 1. Continued/

Compound	Calculated			Experimental a/			Ref.
	E(eV)	f	α^0	E(eV)	$\log \epsilon$	f	
BENZENE-O-DICARBOXYLIC ACID	4.393	0.046	257.8	4.492	3.16	0.035	5
	4.871	0.198	140.1	5.414	3.96	0.219	
	4.965	0.075	353.8				
	5.703	0.616	227.7				
	5.903	0.064	214.7				
	6.275	0.577	251.9				
	6.340	0.629	161.2				
	6.956	0.074	105.8				
BENZENE-M-DICARBOXYLIC ACID	4.454	0.011	165.2	4.396	2.98	0.023	5
	5.251	0.206	248.9	5.390	4.08	0.288	
	5.570	1.048	339.6	5.932	4.59	0.933	
	5.975	0.110	192.5				
	6.181	0.236	294.7				
	6.194	0.406	41.3				
	6.485	0.019	199.4				
	6.641	0.202	256.9				
BENZENE-P-DICARBOXYLIC ACID	4.417	0.043	306.3	4.335	3.23	0.041	6
	4.939	0.813	193.9	5.123	4.21	0.389	
	5.819	0.000	120.0				
	5.975	0.038	281.7				
	6.319	0.665	92.5				
	6.457	0.000	120.0				
	6.619	0.885	185.6				
	6.843	0.000	120.0				
O-NITROBENZOIC ACID	4.255	0.090	83.7	4.275	3.10	0.030	1
	4.604	0.143	155.6				
	4.750	0.152	170.0	5.275	3.82	0.158	
	5.570	0.346	229.4				
	5.702	0.153	245.7				
	5.845	0.210	304.8				
	6.221	0.307	191.6				
	6.678	0.267	287.1				
M-NITROBENZOIC ACID	4.431	0.011	101.9	4.189	2.88	0.018	1
	5.031	0.251	10.2	5.040	3.89	0.186	
	5.468	0.753	145.5	5.661	4.43	0.646	
	5.731	0.223	175.3				
	5.927	0.057	109.9				
	6.050	0.227	263.3				
	6.134	0.127	253.5				
	6.513	0.010	276.7				

/Table 1. Continued/

Compound	Calculated			Experimental ^{a/}			Ref.
	E eV	f	α°	E eV	log ϵ	f	
P-NITROBENZOIC ACID	4.370	0.047	285.7	4.275	3.88	0.058	1
	4.819	0.670	7.3	4.900	4.15	0.339	
	5.688	0.094	284.1				
	5.713	0.032	266.2				
	5.983	0.160	80.6				
	6.148	0.008	18.1				
	6.513	0.367	315.5				
	6.634	0.750	200.9				
O-DINITROBENZENE	4.452	0.070	30.0	4.428	3.14	0.033	1
	4.755	0.020	300.0				
	4.965	0.000	210.1				
	5.052	0.197	300.0	5.166	3.90	0.191	
	5.697	0.645	210.0	5.848	4.19	0.372	
	5.880	0.253	120.0				
	6.035	0.222	120.0				
	6.154	0.164	210.0				
M-DINITROBENZENE	4.495	0.023	150.0	4.350	2.98	0.023	1
	5.174	0.122	240.0				
	5.348	0.725	150.0	5.462	4.33	0.513	
	5.667	0.003	240.0				
	5.724	0.132	330.0				
	5.870	0.301	60.0				
	6.053	0.042	150.0				
	6.081	0.207	240.0				
P-DINITROBENZENE	4.344	0.057	270.0	4.217	3.28	0.046	1
	4.945	0.659	0.0	4.862	4.18	0.363	
	5.502	0.173	90.0				
	5.504	0.000	270.0				
	5.942	0.000	120.0				
	5.997	0.000	120.0				
	6.279	0.157	90.0				
	6.529	0.616	0.0				

NOTE:

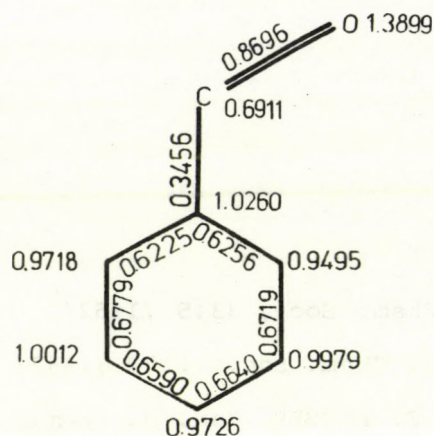
^{a/} The experimental data refer to cyclohexane solution, with the following exceptions: benzene-m-dialdehyde is measured in methanol, benzene-o- and m-dicarboxylic acid in 0.1 N HCl, and benzene-p-dicarboxylic acid in dioxane.

2. REFERENCES

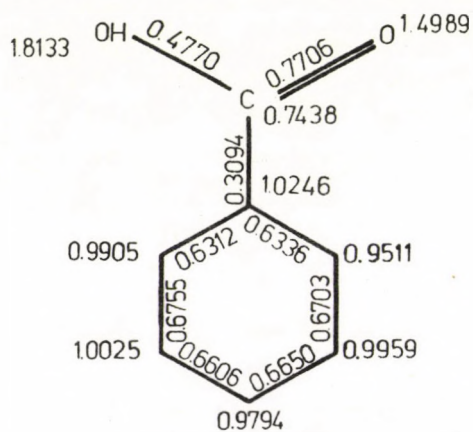
1. Own measurement
2. J.F. GROVE, J. Chem. Soc., 3345 /1952/
3. K.F. JENNINGS, J. Chem. Soc., 1172 /1957/
4. J.C. DEARDEN, W.F. FORBES, Can. J. Chem., 36, 1362 /1958/
5. L. DOUB, J.M. VANDENBELT, J. Am. Chem. Soc., 71, 2414 /1949/
6. B. SEIDEL, Z. Elektrochem., 62, 214 /1958/

3. CHARGE DENSITIES AND BOND ORDERS

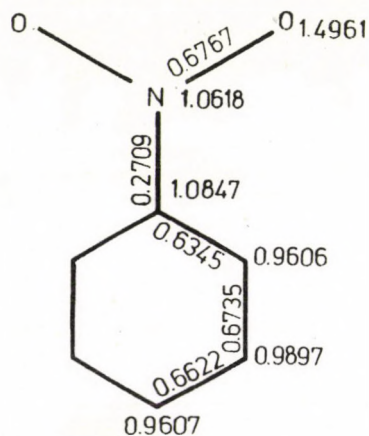
3.1 Benzaldehyde



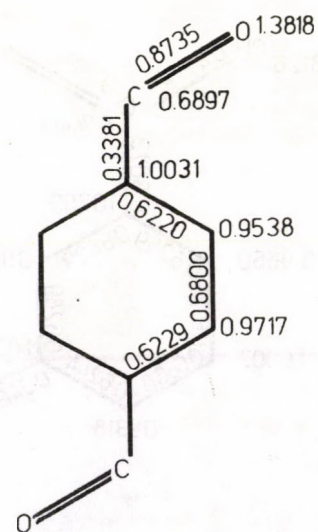
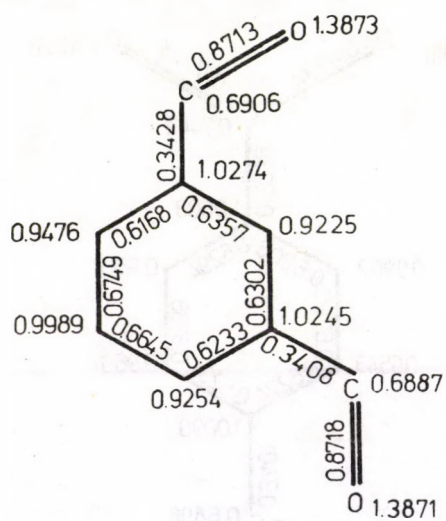
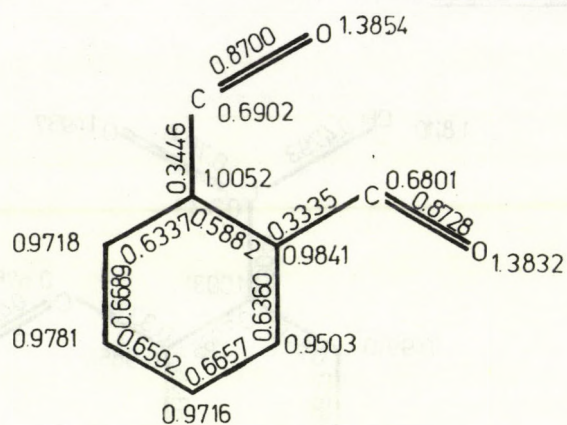
3.2 Benzoic acid



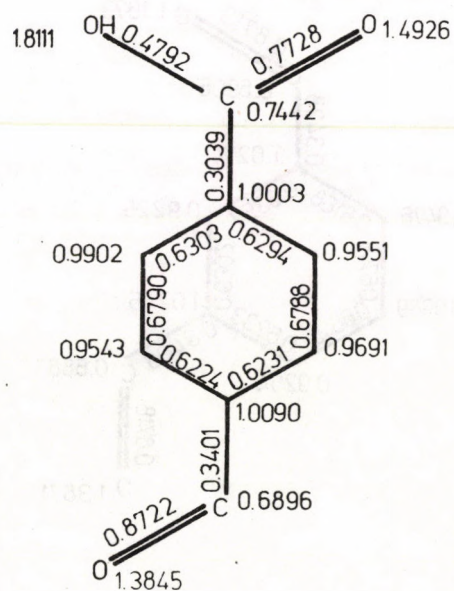
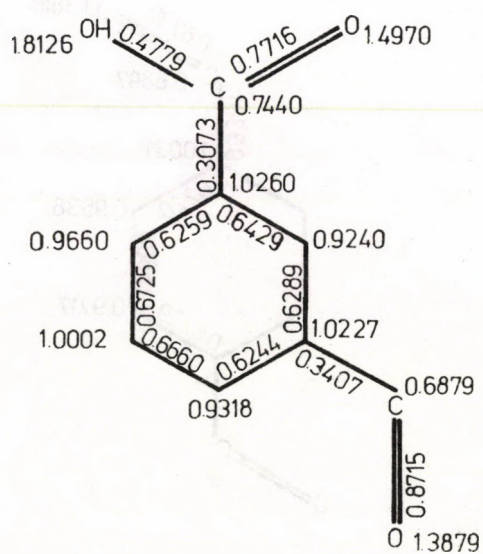
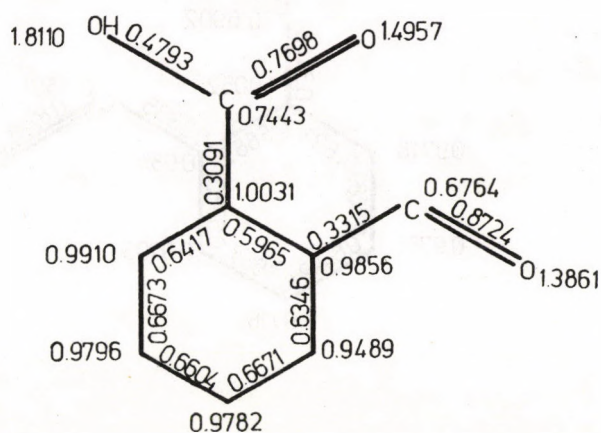
3.3 Nitrobenzene



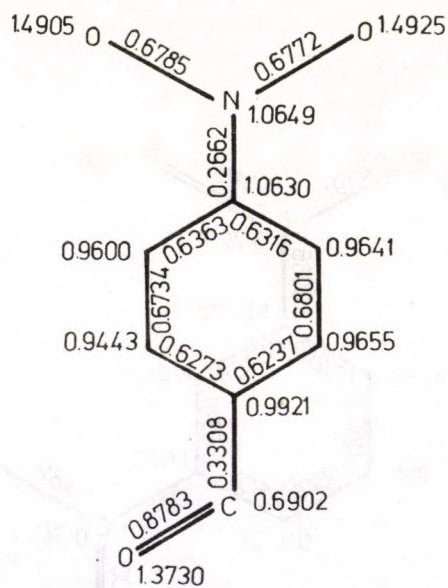
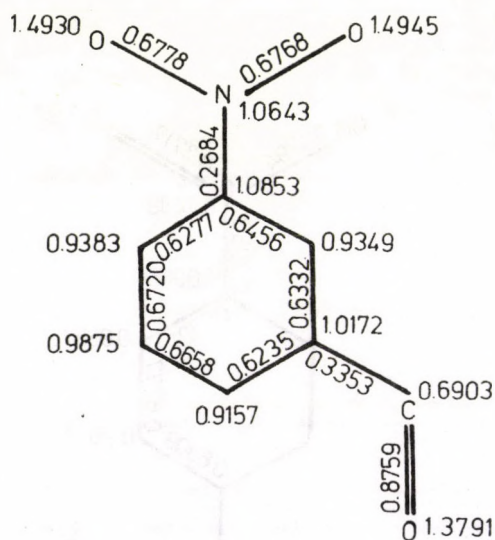
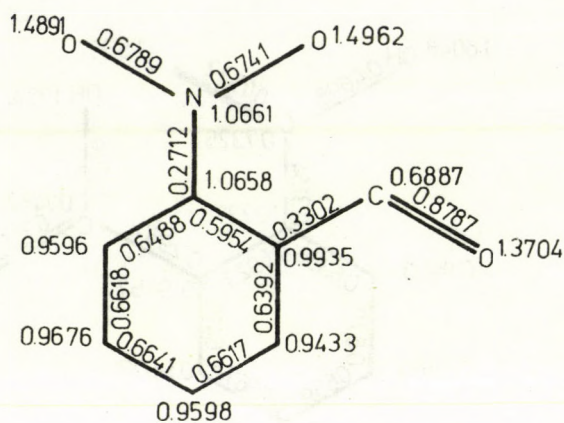
3.4 Benzene-dialdehydes



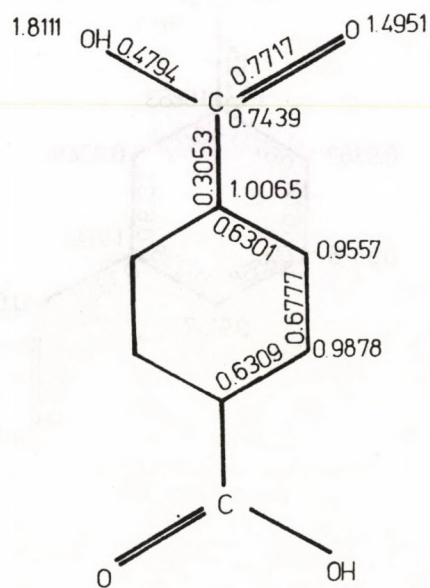
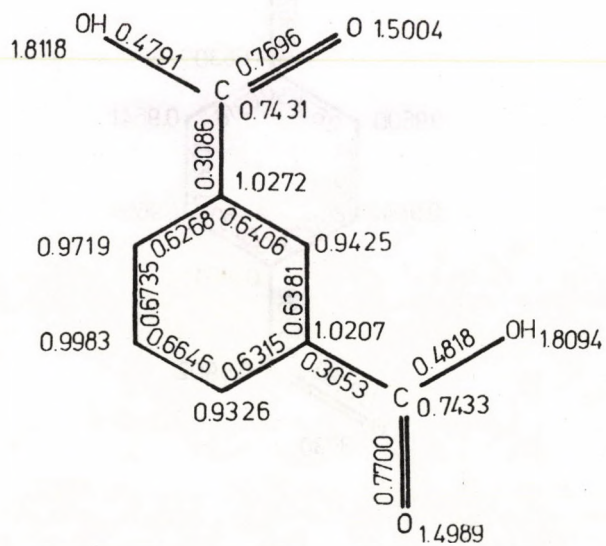
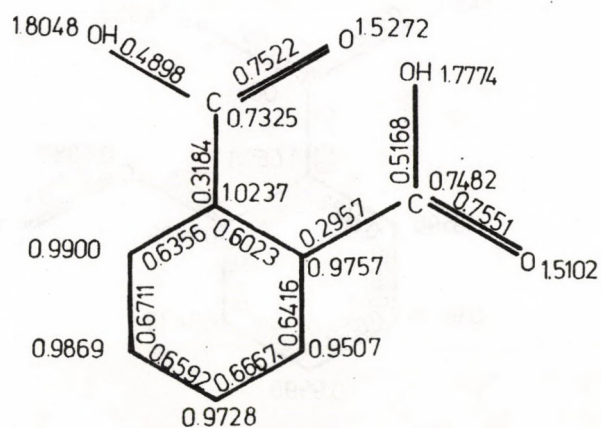
3.5 Formylbenzoic acids



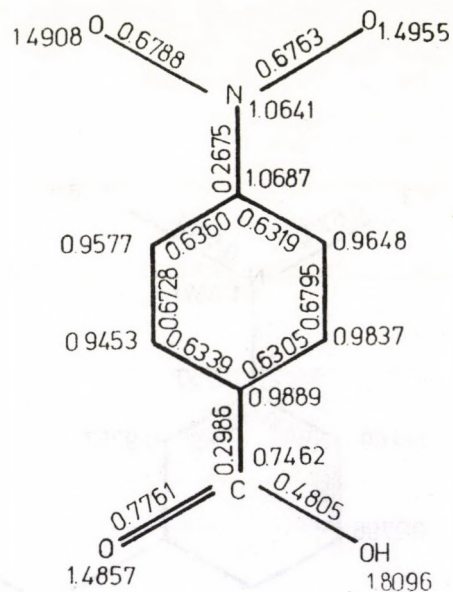
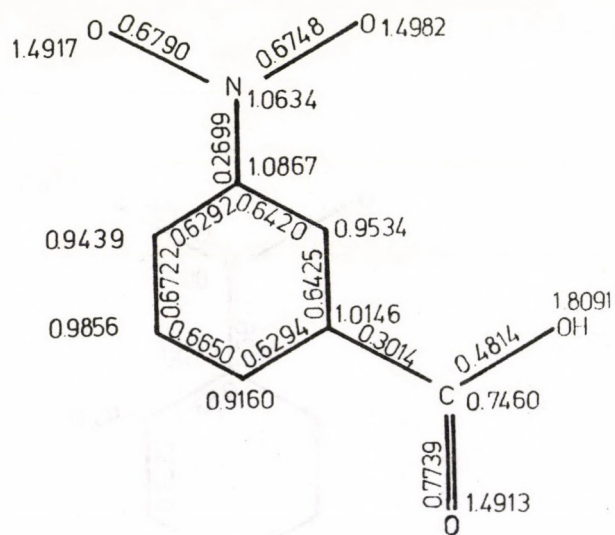
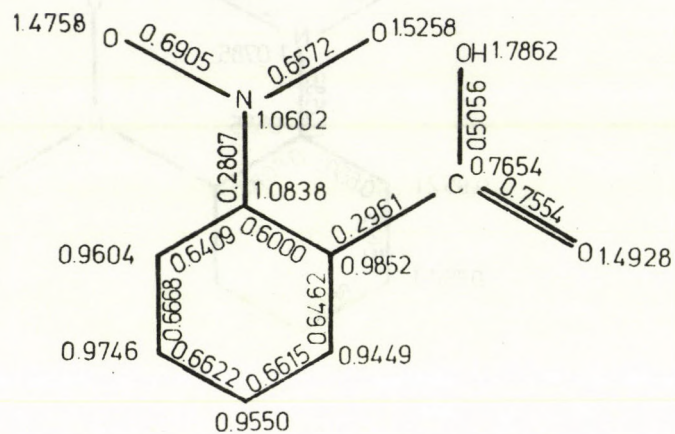
3.6 Nitrobenzaldehydes



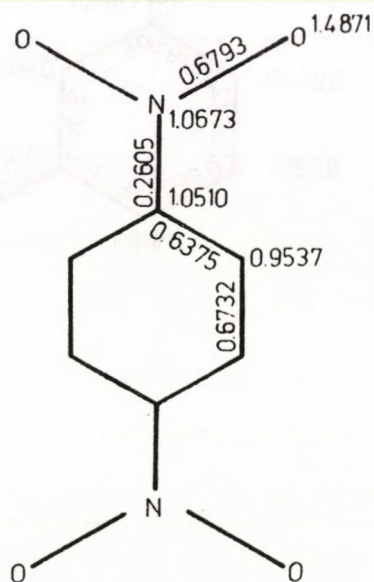
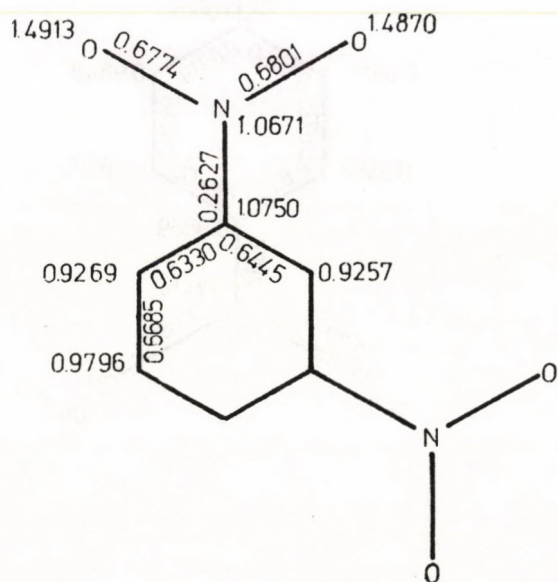
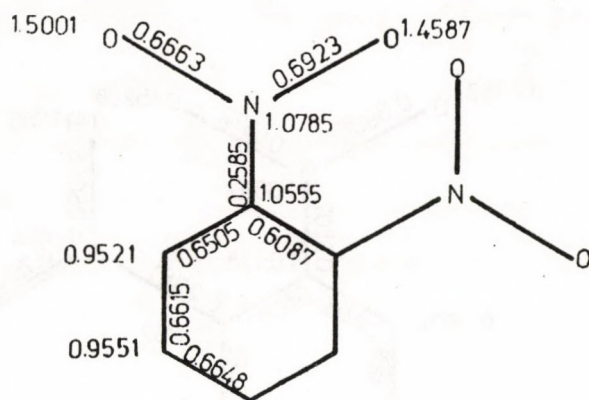
3.7 Benzene-dicarboxylic



3.8 Nitrobenzoic acids



3.9 Dinitrobenzenes



4. CORRELATIONS BETWEEN THE CALCULATED AND EXPERIMENTAL TRANSITION ENERGIES

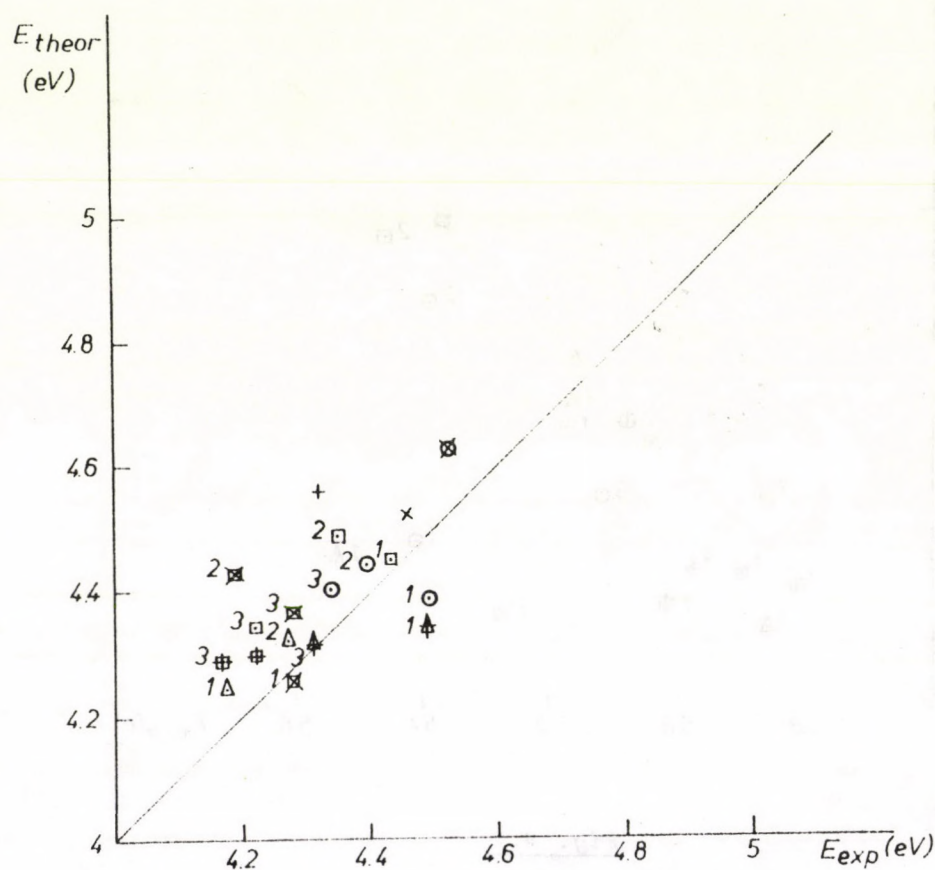


Fig. 4.1

Correlation between the calculated and experimental energy of the α band

\times CHO; \boxtimes COOH; $+$ NO₂; Δ CHO, CHO; \uparrow CHO, COOH;
 \boxplus CHO, NO₂; \odot COOH, COOH; \boxtimes COOH, NO₂; \boxminus NO₂, NO₂

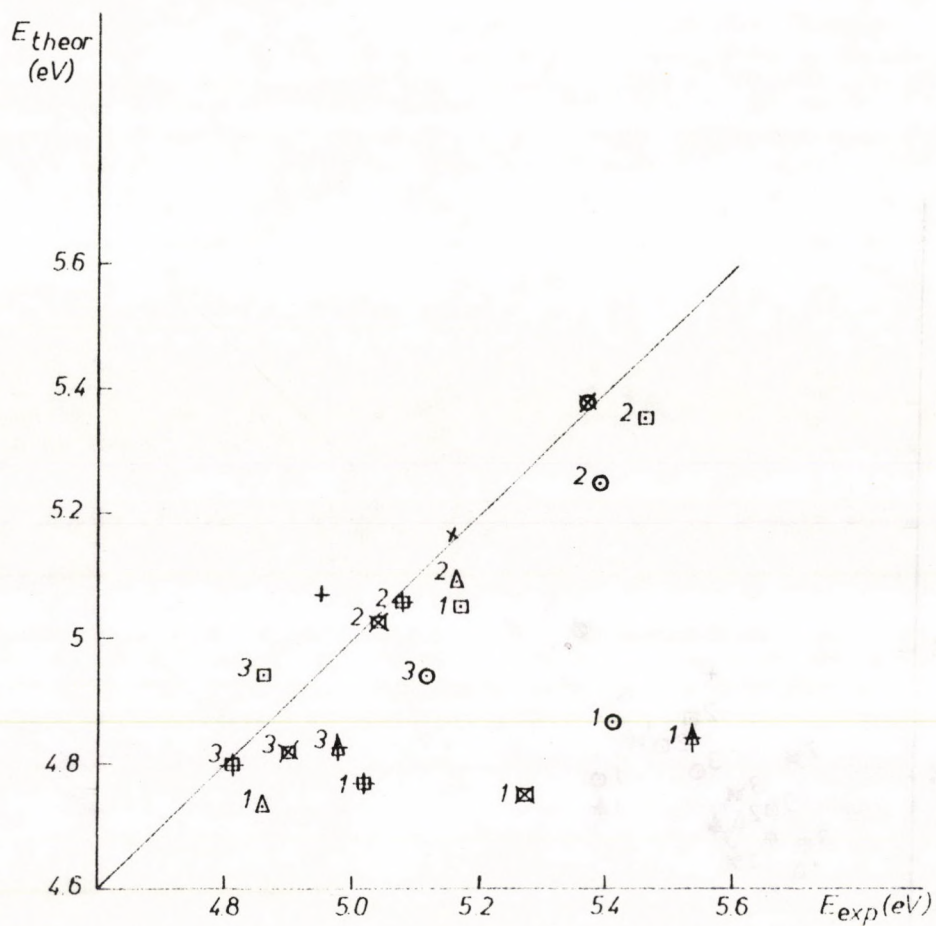
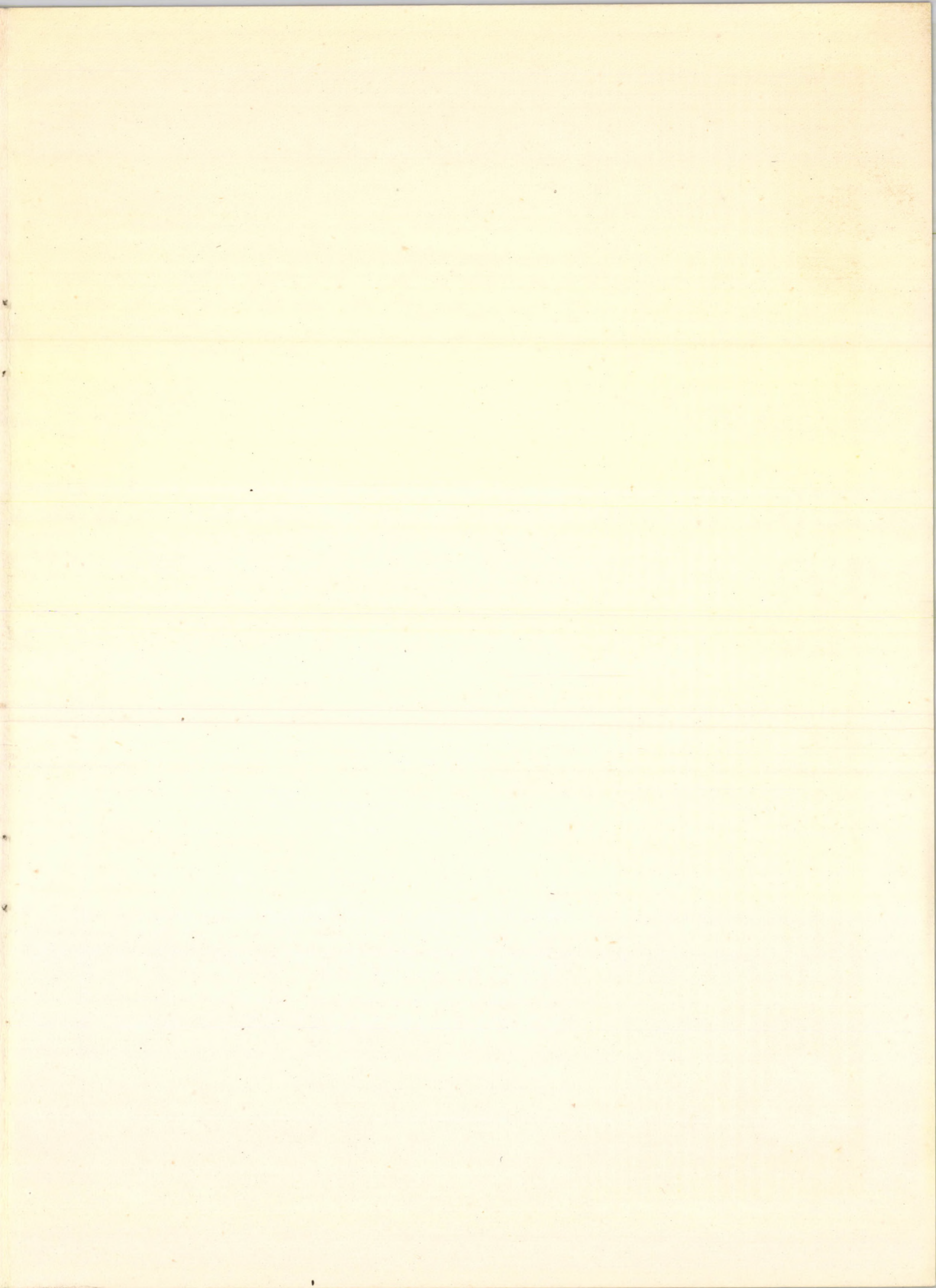


Fig. 4.2

Correlation between the calculated and experimental energy of the p band

For notation see caption of Fig. 1.



61 981



Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Kroó Norbert, a KFKI
Optikai Tudományos Tanácsának elnöke
Szakmai lektor: Kapuy Ede
Nyelvi lektor: T. Wilkinson
Példányszám: 335 Törzsszám: 73-7744
Készült a KFKI sokszorosító üzemében
Budapest, 1973. január hó